

SCIENCE FOR CERAMIC PRODUCTION

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MICROSTRUCTURE AND PROPERTIES OF A MATERIAL BASED ON NATURAL WOLLASTONITE

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The microstructure of a material based on natural wollastonite with different sintering temperatures (850 – 1100°C) is studied. The effect of microstructure on porosity, shrinkage, water absorption, and mechanical strength is studied. The meaning of the physicochemical processes is discussed. The physicomechanical characteristics of the material are described.

Wollastonite (natural calcium metasilicate CaSiO_3) has unique properties and is used as a substitute for asbestos, which is a carcinogenic material.

The purpose of the present study is to investigate the formation of the microstructure of the material at different sintering temperatures (850 – 1100°C) and the effect of the microstructure on porosity, shrinkage, water absorption, and strength.

The microstructure and the phase composition of samples based on natural Indian wollastonite [1] were studied using petrographic analysis [2] in transmitted light on immersion samples and transparent sections employing MIN-8 and POLAM-L-213 polarization microscopes at magnifications up to 1000 times. The results of these studies were refined using x-ray phase analysis.

The phase composition of the initial material is heterogeneous: it is mainly represented by γ -wollastonite crystals of a tabular, frequently elongated idiomorphic shape, up to the needle shape; γ -wollastonite is the triclinic modification with refractive indexes $n_g = 1.633 \pm 0.001$ and $n_p = 1.621 \pm 0.001$ [2]. The size of the needle-shaped crystals varies from 0.5×3 to $7 \times 280 \mu\text{m}$, and the prevailing size is $40 - 70 \mu\text{m}$ long. Along with wollastonite, there are large elongated prismatic crystals of natural enstatite of size up to $30 \times 150 \mu\text{m}$ constituting a solid solution FeSiO_3 based on the compound $\text{Mg}_2[\text{Si}_2\text{O}_6]$ of the rhombic symmetry with $n_g = 1.666 \pm 0.001$ and $n_p = 1.656$. For this type of solid solution with the specified optical constants the quantitative ratio of cations in the solid solution $\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+})$ is 0.87 [2].

The microstructure of the wollastonite material after sintering at 850°C (Fig. 1) has a heterogeneous phase and chemical composition. The main crystalline phase is γ -wollastonite of the triclinic modification; β -parawollastonite of the monoclinic modification is represented by needle-shaped crystals of a regular idiomorphic prismatic shape with $n_g = 1.631$, $n_p = 1.614$, and $n_m = 1.629$ [2] with an average particle size of $30 \times 105 \mu\text{m}$. Furthermore, there are large idiomorphic crystals of elongated prismatic and needle shapes that form aggregates of a columnar structure with mutual penetration of the constituent elements.

Porosity in ceramics is distributed nonuniformly: there are zones of pore aggregation and totally pore-free zones. The latter well-sintered zones typically have a coarse-crystalline structure of regularly grown together crystals of the solid solution $\text{FeO} \cdot \text{SiO}_2$ based on rhombic enstatite and monoclinic pyroxene in the form of diopside $\text{Mg, Ca}[\text{Si}_2\text{O}_6]$ with $n_g = 1.695$, $n_p = 1.666$, and $n_m = 1.672$. The average size of the prismatic enstatite crystals is $35 \times 160 \mu\text{m}$. Occasional crystals reach a size of $50 \times 160 \mu\text{m}$. Single crystals of size $14 \times 26 \mu\text{m}$ are found. There are as well large diopside crystals of a prismatic shape. The vitreous phase present in the material cements the crystalline structural components and forms zones of their predominant aggregation.

As the sintering temperature grows to 900°C, the phase composition of the material is preserved, the processes of compaction and crystallization of the material are intensified and the large enstatite crystals grow, while the fine needle-shape wollastonite crystals disappear. The average size of the needle-shape wollastonite crystals is $1 \times 40 \mu\text{m}$ and that of

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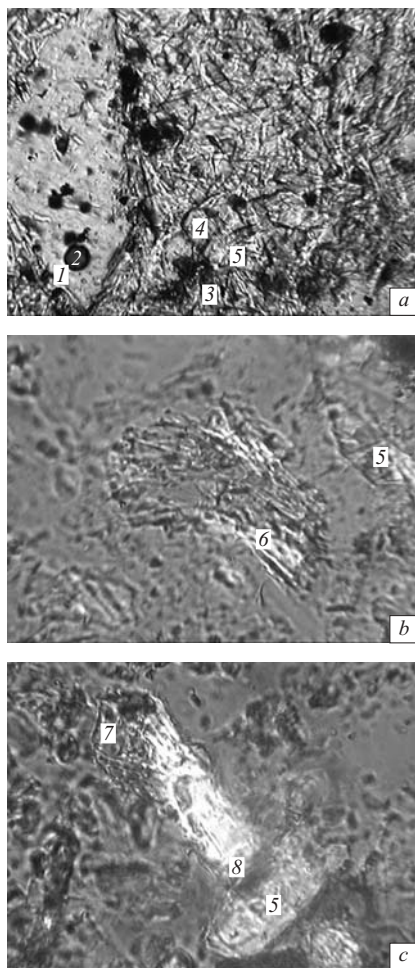


Fig. 1. Microstructure of wollastonite material after sintering at 850°C (transparent section, transmitted light): *a*) magnification $\times 190$; *b*, *c*) magnification $\times 470$; 1) vitreous phase; 2) pore; 3) fiber (needle); 4) concretion of enstatite and diopside; 5) enstatite; 6) fiber concretion; 7) wollastonite fiber; 8) crystal concretion.

the solid solution crystals based on rhombic enstatite $\text{Mg}_2[\text{Si}_2\text{O}_6]$ is $40 \times 160 \mu\text{m}$.

The microstructure of the wollastonite material after sintering at 1000°C is characterized by interweaving of the needle crystals of γ - and β -wollastonite. An increase in the firing temperature to 1000°C is accompanied by a more intense transformation of γ -wollastonite into β -parawollastonite. In doing so, the quantity and size of fine needle-shaped wollastonite crystals decreases compared to the material fired at 900°C. The needle-shaped crystals are on the average 20 μm long. The sizes of the prismatic enstatite crystals vary insignificantly. The average size of these crystals is $50 \times 170 \mu\text{m}$.

The microstructure of the wollastonite material after sintering at 1100°C is indicated in Fig. 2. The main crystalline phase is β -wollastonite. γ -Wollastonite is present in smaller quantities. As the firing temperature grows to 1100°C, the tendency of active transformation of γ -wolla-

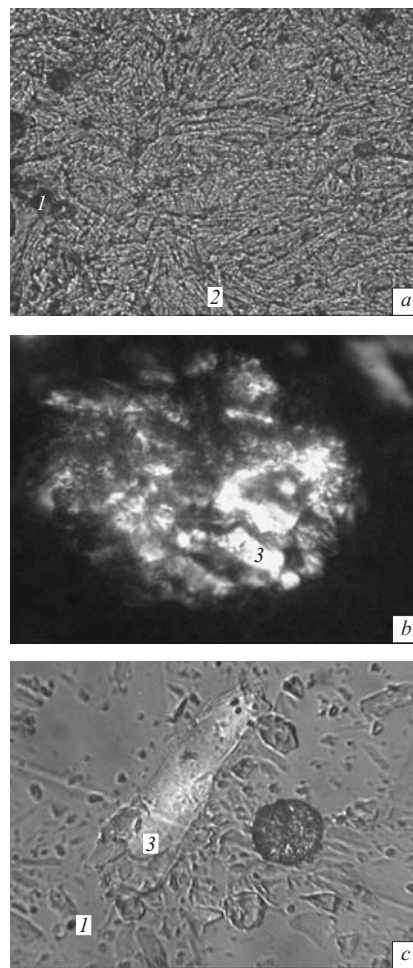


Fig. 2. Microstructure of wollastonite material after sintering at 1100°C (transparent section, transmitted light): *a*) magnification $\times 200$; *b*, *c*) magnification $\times 470$; 1) pore; 2) fiber; 3) concretion of crystals.

stonite into β -parawollastonite is more evident than the processes of polymorphic transformation of wollastonite considered above. A certain amount of fine needle-shaped β -wollastonite crystals with an average needle size of $0.5 \times 13 \mu\text{m}$ is present in the free state. Concretions of β -parawollastonite, pure enstatite, and solid solutions based on them are formed. The overall presence of prismatic crystals with $n_g = 1.658$, $n_p = 1.650$, and $n_m = 1.653$ belonging to pure rhombic enstatite indicate the disintegration of the solid solution at 1100°C with the formation of pure enstatite and fayalite $\text{Fe}_2[\text{SiO}_4]$, which, in turn, decomposes into FeO and SiO_2 in an amorphous jelly-like form and activates the sintering of the material. Pore-free well-sintered crystals concretions reach the size of 185 μm .

The material is better sintered and has a coarse-crystalline structure with penetrating prismatic crystals. The aggregates (concretions) of columnar shape consist of prismatic β -parawollastonite, enstatite, and diopside crystals.

TABLE 1

| Sintering temperature, °C | Average crystal sizes, μm | | Average density of fired sample, g/cm^3 | Porosity, % | | Shrinkage, % | | Water absorption, % | Compression strength MPa |
|---------------------------|--------------------------------------|-----------------|---|-------------|------|--------------|-----------|---------------------|--------------------------|
| | wollastonite | enstatite | | open | true | in diameter | in height | | |
| 850 | 30×105 | 35×160 | 1.57 | 45.0 | 45.1 | 3.8 | 5.4 | 28.8 | 57.6 |
| 900 | 1×40 | 40×160 | 1.63 | 42.6 | 42.9 | 4.8 | 13.4 | 26.2 | 59.6 |
| 1000 | Up to 20* | 50×170 | 1.93 | 32.4 | 32.5 | 9.6 | 17.1 | 16.9 | 82.9 |
| 1050 | — | — | 2.00 | 27.5 | 29.3 | 14.4 | 20.5 | 14.3 | 151.9 |
| 1100 | 0.5×13 | 55×180 | 2.32 | 1.1 | 18.6 | 16.4 | 22.9 | 0.7 | 163.8 |

* In length.

X-ray phase analysis corroborated the presence of phases identified by the petrographic method.

The research indicated that the material produced by sintering natural wollastonite consists of several crystalline phases and a vitreous phase. The microstructure of the material exhibits regular accretions of wollastonite crystals of predominant needle shape, thickness about $1 \mu\text{m}$ and length $40 - 70 \mu\text{m}$ (Figs. 1a and b, and 2a), and crystals of recrystallized enstatite and diopside of thickness $35 - 55 \mu\text{m}$ and length $160 - 180 \mu\text{m}$, and their concretions reaching $185 \mu\text{m}$ (Figs. 1c and 2b and c) cemented by the vitreous phase formed due to the disintegration of natural enstatite contained in the form of impurity in the initial material from India.

It has been established that the following processes take place as the temperature rises from 850 to 1100°C :

- polymorphic transformation of wollastonite from the triclinic γ -form into the monoclinic β -form;
- decomposition of the solid solution in the system $\text{Mg}_2[\text{Si}_2\text{O}_6] - \text{FeSiO}_3$ constituting natural enstatite crystals and the formation of pure rhombic enstatite and amorphous colloid-like SiO_2 that activates the processes of sintering and recrystallization;
- intensification of recrystallization, formation of enstatite, wollastonite, and diopside concretions.

Changes in the microstructure of the material depending on sintering temperatures modify its physicomechanical properties (Table 1).

It can be seen that with increasing sintering temperature the size of the needle-shaped wollastonite crystals decreases, single enstatite crystals grow from 160 to $180 \mu\text{m}$ long and interweave and, accordingly, the material is compacted and its mechanical strength grows from 57.6 to 163.8 MPa at a temperature of 1100°C .

The increase in the strength of the material with increasing sintering temperature is due to the more intense formation of neogenes reinforcing the vitreous phase in the zones of its aggregation and the strengthening of the contacts between the crystals cemented by the vitreous phase arising as a consequence of the disintegration of solid solutions, which leads to the formation of a composite material based on crystalline and melt-like phases. The needle-shaped crystals of fibrous natural wollastonite (Figs. 1a and b, and 2a), as well as

large enstatite crystals and its concretions with other phases (Figs. 1c and 2b and c), actively enter into reactions and interweave, cementing the structure, which contributes to a rise in the density and mechanical strength of the material with increasing sintering temperature.

It is known [3, 4] that fine particles in sintering with the participation of the liquid phase dissolve in the liquid phase and gradually become smaller in size, whereas the excessive dissolved material precipitates on larger particles and causes their growth. Similarly, fine wollastonite crystals due to diffusion processes with the participation of the liquid phase facilitate the recrystallization process, increasing the size of the crystals.

Liquid-phase sintering is determined by the presence of a special sintering glass additive that forms low-melting eutectics with a melting point of $400 - 1100^\circ\text{C}$ [5, 6], as well as by the formation of SiO_2 from natural enstatite crystals in sintering.

Silicate systems typically form metastable compounds that transform into a stable crystalline state with minimum free energy [7]. The recrystallization of a material based on phases with the same crystalline structure under slow cooling leads to the formation of continuous series of metastable solid solutions. The decomposition of enstatite-based solid solutions in heating is presumably related to the specifics of the behavior of silicate systems in cooling commented in [7]. This, in turn, contributes to a corresponding increase in the mechanical strength of the material after sintering at the specified temperatures.

The above studies of the microstructure and phase composition of the material establish that a temperature increase within the interval of $850 - 1100^\circ\text{C}$ facilitates the growth of enstatite crystals and its concretions. The growth of enstatite crystals due to the dissolution of fine needle-shaped wollastonite crystals, in turn, facilitates the formation of crystalline concretions and strengthening of the material. A heat-insulating material with an optimal structure and physicomechanical properties has been obtained by sintering at 850°C . Sintering proceeds with the participation of the liquid phase formed by low-melting eutectics from the components of the special sintering glass additive. This material is based on wollastonite; enstatite and its concretions, as well as the vitreous phase, are present in smaller quantities. The

microstructure of the material is characterized by regular coalescence of wollastonite crystals with enstatite and other crystalline phases cemented by the vitreous phase.

Wollastonite samples exhibit a higher resistance in aluminum alloy melts than asbestos-bearing materials. Thus, the material obtained can be recommended for making heat-insulating parts (sleeves, bushes, plates) for discharging and transportation of aluminum alloys.

REFERENCES

1. N. I. Demidenko and E. S. Konkina, "Sintering of wollastonite mixtures based on natural wollastonite," *Steklo Keram.*, No. 1, 15 – 16 (2003).
2. A. Winchell and H. Winchell, *The Microscopical Characters of Artifician Inorganic Solid Substances: Optical Properties of Artificial Minerals*, New York (1964).
3. V. A. Ivansen, *Phenomenology of Sintering* [in Russian], Metallurgiya, Moscow (1985).
4. V. N. Eremenko, Yu. V. Naidich, and I. A. Lavrinenko, *Sintering in the Presence of a Liquid Metallic Phase* [in Russian], Naukova Dumka, Kiev (1968).
5. E. Morris, "Fine precipitation in crystalline ceramics," *Ceram. Bull.*, **51**(6), 510 – 515 (1972).
6. I. A. Toropov, V. P. Barzakovskii, V. V. Lapin, and N. N. Kurtseva, *Phase Diagrams of Silicate Systems* [in Russian], Nauka, Moscow – Leningrad (1965).
7. V. P. Barzakovskii, V. V. Lapin, A. I. Boikova, and N. N. Kurtseva, *Phase Diagrams of Silicate Systems* [in Russian], Nauka, Leningrad (1974).